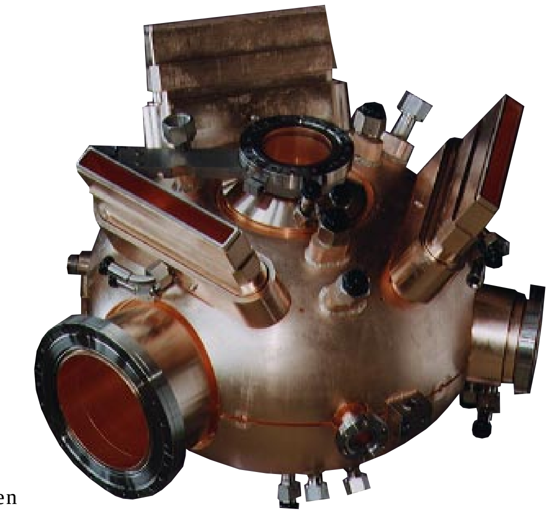
Plating Shop Moves to Finish Off Waste



One of the two dozen radiofrequency cavities coated with copper by the Laboratory's Chemical and Electrochemical Processes Facility as part of our work on the Stanford Linear Accelerator Center's "B-factory." The cavities are 60 cm in diameter and 35.6 cm tall.

WHEN physicists at Stanford Linear Accelerator Center's "B-factory" last year needed to coat two dozen 35.6-cm-tall cavities with pure copper and ultraclean some 50,000 other parts for a set of unprecedented high-energy experiments, they turned to specialists at the Lawrence Livermore Chemical and Electrochemical Processes Facility.

The facility is operated by the Metal Finishing Group of Mechanical Engineering's Manufacturing and Materials Engineering Division. Over the past three decades, the facility has earned a reputation as one of the top-flight metal finishing centers in the nation, using chemical and electrochemical processes for wide-ranging assignments from LLNL research programs, other national laboratories, and international research agencies such as CERN (the European high-energy physics research organization).

During the past few years, the facility has also made a name for itself by embracing environmentally conscious manufacturing principles. Working in stages, the shop has adopted scores of improvements that included recycling strong acids, substituting Earth-friendlier materials, and eliminating cyanide in its operations. The advances have been made as part of a larger, Laboratory-wide effort to encourage pollution prevention and waste minimization activities.

The operation's environmental efforts have been so successful that the facility has decreased its discharge of water to the Livermore sewer system from 11.4 million liters (3 million gallons) to zero! And whereas in 1991 the facility was producing 227,100 liters (60,000 gallons) of chemical waste to be trucked off site, it now produces only 3,785 liters (1,000 gallons) of this waste annually, a dramatic reduction.

As a result of these accomplishments, plating shop personnel are sharing lessons learned with both Department of Energy centers and private firms on how to respond to tightened environmental regulations and waste disposal costs by minimizing wastes and substituting better procedures.

The products of chemical and electrochemical finishing are found throughout modern society, from galvanized nails to shiny chrome-plated faucets, from automobile trim to the gold and silver electrical contacts in computers and telephones. Such finished parts can be stripped and replated if they tarnish, scratch, or wear out. However, heavy metals, toxic chemicals, and large volumes of waste (much of it hazardous) for many years seemed an inescapable part of the metal finishing business at the Laboratory and elsewhere.

But that assumption changed for Livermore in the late 1980s, according to Jack Dini, Materials Engineering and Mechanics section leader, when the Chemical and Electrochemical Processes Facility began to scrutinize its operations with an eye on minimizing waste and preventing pollution. The in-depth look was prompted by stiffer regulations, higher costs to dispose of wastes, a growing environmental consciousness, and the appearance of new techniques in the marketplace that used fewer hazardous materials and produced less hazardous wastes. The result was modification of many operations over several years, but most importantly, says Dini, the adoption of a different mindset centered on incorporating environmental consciousness in every facet of the facility's operations.

"Today we have a safer and cleaner facility, produce much less pollution, and have maintained the quality of parts processed through our operation," Dini says. "Being in the forefront of both metal finishing technology and waste minimization is not only possible, but they go hand in hand."

What's more, the environmental changes have produced sizable cost savings. Today the facility is saving more than $500,000 per year. According to Chris Steffani, shop supervisor, many of the savings resulted from relatively simple material substitutions. For example, costly chlorinated cleaning compounds were replaced with much cheaper, and more environmentally kind, materials. For more thorough cleaning, high frequency sound waves remove very fine particulates, and the residual water is recycled for another round of cleaning chores.

Because wastewater typically represents the largest waste stream, shop personnel have given it very high priority. Material discharged to municipal sewers must meet strict guidelines, and wastes that must be trucked off site cost at least 75¢ per liter ($3 per gallon) for transport, treatment, and disposal. Standard degreasing equipment was replaced with a variety of aqueous cleaning processes including soak and electrolytic cleaning and ultrasonic cleaning (mentioned above). These were connected to a rinse water recycling system capable of recycling 2,840 liters (750 gallons) a day. The recycled water is further purified by an ion exchange unit for operations other than simple rinsing.

As a result of these actions, the facility is saving over 11.4 million liters (3 million gallons) of water per year and no longer sends any water to the City of Livermore's sewer system. What's more, the shop's recycled water has fewer metallic ions than the water supplied to city residents. Nominated by the City of Livermore, the Laboratory received a 1993 award in recognition of these accomplishments from the California Water Pollution Control Association.

Dealing with Acids

Minimizing the use and waste of inorganic acids has been one of the facility's largest concerns. Such acids are commonly used in shops to remove surface blemishes, produce bright surfaces, strip unwanted metals and coatings, and prepare metal surfaces to receive other coatings. The acids are also used as electrolytes for coatings produced by electrolytic oxidation such as anodizing. Eventually the acids become unusable or weakened because of contamination with metals or the conversion of hydrogen ions into hydrogen gas. The acid then becomes waste and a new acid batch is started.

The facility installed diffusion dialysis equipment to recover acids and separate the metal component for recovery and sale to refineries. The equipment uses a new kind of membrane that can withstand low pH solutions. Using this system, the facility now recycles spent solutions of nitric, sulfuric, and hydrochloric acids with a recovery efficiency of about 80%.

In addition, the facility is now using ferric sulfate material to clean aluminum parts as a substitute for a process that used concentrated acids. The new solution lasts much longer and does not cause a problematic insoluble aluminum fluoride film that formed with the acid process.

Also, the facility substituted oxalic acid for sulfuric acid when anodizing aluminum. Because oxalic formation is much less corrosive than sulfuric acid, equipment, floors, and tanks last much longer. As an added bonus, anodized aluminum coatings with oxalic acid are much smoother.

Another approach to minimize waste has been to extend the life of materials. A case in point is electroless nickel solutions, widely used to coat a variety of surfaces by immersion in a bath containing a chemical reducing agent. The solutions have a tendency to spontaneously plate out on the tank and associated equipment, adding to the plating cost. Also, expensive treatment is required before the spent solution can be disposed of. In response, Steffani and his technicians incorporated an electrodialysis process that reduces both chemical purchases and disposal costs. The technology separates dissolved solids from the nickel ions, making it possible to reuse the tanks many times without disposal. The electrodialysis operation is simple and runs virtually unattended.

Substituting New Technologies

One of the most important materials substitutions was made for hexavalent chromium plating, until recently the standard chromium plating process. This process generates air emissions, effluent rinse water, and solutions that are toxic and suspected of being carcinogens. Facility people estimated that it would cost about $25,000 to demonstrate compliance with

Kelye Allen of Livermore's plating shop plates (left) a metal bellows component to be used in the Laboratory's lasers program with an environmentally friendly nickel–tungsten–boron deposit, which replaces hexavalent chromium, a plating material that is a source of toxic and possibly carcinogenic air and water pollutants. On the right, she rinses off excess nickel–tungsten–boron material with water that is treated and reused.

tougher Bay Area Air Quality Management District regulations on emissions from hexavalent chromium and that compliance costs would mount in future years.

As a result, the facility adopted a compound composed of 59.5% nickel, 39.5% tungsten, and 1% boron as a substitute for hexavalent chromium. The new material has excellent wear, corrosion resistance, and mechanical properties. It also poses less of an environmental risk and reduces energy costs.(See the photos on p. 29.)

Much of the effort to adopt more environmentally friendly procedures and materials has centered on cyanide. Because of the hazardous nature of cyanide, extensive safety precautions must be incorporated when manufacturing the electroplating chemicals, transporting them to user sites, using the electroplating process, and disposing of wastes. For example, if cyanide-based solutions become too acidic, large amounts of poisonous cyanide gas are liberated. The electroplating industry as a whole has suffered many accidents—and a few deaths—from cyanide use. In addition, cyanide use costs more—disposal costs for LLNL wastes containing cyanides are about $1.50 per liter ($6 per gallon) compared to 75¢ per liter ($3 per gallon) for noncyanide wastes.

Over the past several years, the Livermore facility found substitutes for almost every process involving cyanide. For example, copper cyanide plating was replaced with a copper pyrophosphate process. The substitution works quite well and produces parts as good as those obtained with the copper cyanide process.

Until recently, silver was the remaining metal still relying on cyanide formulations for electrodeposition of lasting and relatively thick deposits. In fact, silver–cyanide plating solutions are the most highly concentrated cyanide solutions used in the plating industry.

In the spring of 1995, LLNL entered into a $2-million Cooperative Research and Development Agreement (CRADA) with Technic Inc. of Providence, Rhode Island, with the goal of providing industry with an environmentally benign alternative to the silver–cyanide plating process for depositing thicknesses greater than 250 micrometers. Laboratory researchers have obtained stress and hardness data and have analyzed the structure of the deposit with metallography and x-ray diffraction. The results show that the electroplating industry for the first time can confidently plate silver with a process that uses no cyanide.

The CRADA effort has been so successful that the Laboratory has nominated our partner for a President's Green Chemistry Challenge Award, a program sponsored by a voluntary partnership of industry, the American Chemical Society, the Council for Chemical Research, and the U.S. Environmental Protection Agency. This awards program recognizes fundamental breakthroughs in chemistry that are useful to industry and accomplish pollution prevention through source reduction.

Helping Small Firms

Another successful collaboration is with the Northern California Association of Metal Finishers. This partnership, sponsored by the LLNL's Small Business Initiative, established a Model Metal Finishing Facility at the Laboratory's Chemical and Electrochemical Processes Shop to assist regional businesses in acquiring and implementing chemical processing technology and providing waste minimization consultation.

Steffani handles calls daily from small metal finishers with questions on minimizing waste or about technical processes. Many calls result in immediate solutions. Other calls involve a request to tour the Laboratory facility or to use the model facility for a few days to work on a new process. Steffani has toured more than 70 small electroplating facilities and helped many of them set up waste minimization programs of their own.

A new partnership is with the U.S. Environmental Protection Agency's Common Sense Initiatives, a program aimed at enhancing interaction between business and the EPA. In a $300,000 project supported jointly by EPA and LLNL's Small Business Office, the Chemical and Electrochemical Processes Shop is selecting four to five projects aimed at helping small electroplating businesses establish waste minimization and pollution prevention programs. Dini notes that a third of the nation's small electroplating firms have gone out of business in recent years largely because of the burden of meeting environmental regulations.

To date, the shop's largest partnership is with Stanford Linear Accelerator Center (SLAC), Lawrence Berkeley National Laboratory, and other LLNL programs to design and build the so-called "B-factory" (named after the elusive B-meson subatomic particle) at SLAC. (See the photo on p. 28.) The shop is receiving $750,000 for ultracleaning some 50,000 parts that make up 1,400 ion pumps and for copper coating 300 meters of connecting pipe and two dozen, 60-cm-diameter, 35.6-cm-tall radio-frequency cavities that will keep electrons traveling at nearly the speed of light.

Key Words: metal finishing—chemical and electrochemical processes, electroplating; pollution prevention; waste minimization.

For further information contact Jack Dini (510) 422-8342 (dini1@llnl.gov) or Chris Steffani (510) 423-1780 (steffani1@llnl.gov).

Patents

Each month in this space we report on the patents issued to and/or the awards received by Laboratory employees. Our goal is to showcase the distinguished scientific and technical achievements of our employees as well as to indicate the scale and scope of the work done at the Laboratory.

Patent issued to	Patent title, number, and date of issue	Summary of disclosure
Daniel D. Dietrich Robert F. Keville	**Electron Source for a Mini Ion Trap Mass Spectrometer** U.S. Patent 5,477,046 December 19, 1995	An integrated electron source and mass analyzer/detector with miniature ion cyclotron resonance mass spectrometer (MS) having low power consumption and ion trap MS that Fourier analyzes the ion cyclotron resonance signals induced in the trap electrodes. This portable, low-power MS with integrated sensors and electronics can detect environmental pollutants and illicit substances.
Thomas E. McEwan	**High Speed Sampler and Demultiplexer** U.S. Patent 5,479,120, December 26, 1995	A demultiplexer based on a plurality of banks of samplers (each bank comprising transmission lines for transmitting an input signal) and strobe signal and sampling gates at respective positions for sampling the input signal in response to the strobe signal. Strobe control circuitry is coupled to the plurality of banks and supplies a sequence of bank strobe signals to the strobe transmission lines.
Ger Van den Engh Richard J. Esposito	**Multiple Sort Flow Cytometer** U.S. Patent 5,483,469 January 9, 1996	A flow cytometer with means for deflecting and focusing charged droplets into multiple streams. A pair of oppositely charged plates disposed on each side of a droplet flow with a respective ground plane for each plate produce a curved and focused electric field between the plates to more accurately focus deflections of the charged droplets.
Robert J. Contolini Steven T. Mayer Lisa A. Tarte	**Removal of Field and Embedded Metal by Spin Spray Etching** U.S. Patent 5,486,234 January 23, 1996	A process for uniformly removing metal from a substrate surface and above metal-containing trenches formed in the substrate for producing an essentially planar surface across the substrate and the trenches. The surface is rotated while directing an etchant onto the surface.
Troy W. Barbee, Jr. Gary W. Johnson Dennis W. O'Brien	**High Performance Capacitors Using Nano-Structure Multilayer Materials Fabrication** U.S. Patent 5,486,277 January 23, 1996	The fabrication of high energy–density capacitors by nano-engineered, multilayer synthesis technologies, whereby the materials, thickness of layers, interfacial quality, and conductor configuration can be precisely controlled. Magnetron sputtering of very thin conductive and dielectric layers is used.
Margaret L. Carman Kenneth J. Jackson Richard B. Knapp John P. Knezovich Nilesh N. Shah Robert T. Taylor	**Methods for Microbial Filtration of Fluids** U.S. Patent 5,487,834 January 30, 1996	A method for purifying contaminated subsurface groundwater by contacting the contaminated subsurface groundwater with resting state methanotrophic or heterotrophic microorganisms that produce long lifetime contaminant-degrading enzymes. The micro-organisms are derived from surface cultures and are injected into the ground to act as a biofilter. The contaminants include organic or metallic materials and radionuclides.
Anthony M. McCarthy	**Silicon on Insulator with Active Buried Regions** U.S. Patent 5,488,012 January 30, 1996	A method for introducing patterned buried components in a silicon layer and forming contacts for the buried components in the thin silicon layer after fabrication of the silicon-on-insulator (SOI). This process can be accomplished by using excimer laser-doping techniques during the formation of the SOI and after the SOI has been fabricated. This method applies to SOI wafers made from a silicon wafer bonded to a substrate such as glass or an oxidized silicon wafer.